Discrimination Performance and Exploitation of Spatiotemporal Information and Geometric Optimization of Signal/Noise Performance Using Arrays of Carbon Black-Polymer Composite Vapor Detectors

Shawn Briglin,[1] Michael Burl,[1] Michael Freund,[1]
Phil Tokumaru,[1] Thomas Vaid[1] and Nathan Lewis[1]
[1]Division of Chemistry and Chemical Engineering,
California Institute of Technology
127-72 Noyes Laboratory
Pasadena, Caltech (MS 127-72) 91125
USA

We have investigated various aspects of the geometric and spatiotemporal response properties of an array of sorption-based vapor detectors. The detectors of specific interest are composites of insulating organic polymers filled with electrical conductors, wherein the detector film provides a reversible dc electrical resistance change upon the sorption of an analyte vapor. An analytical expression derived for the signal/noise performance as a function of detector volume implies that there is an optimum detector film volume which will produce the highest signal/noise ratio for a given carbon black-polymer composite when exposed to a fixed volume of sampled analyte. This prediction has been verified experimentally by exploring the response behavior of detectors having a variety of different geometric form factors. We also demonstrate that useful information can be obtained from the spatiotemporal response profile of an analyte moving at a controlled flow velocity across an array of chemically identical, but spatially nonequivalent, detectors. Finally, we demonstrate the use of these design principles, incorporated with an analysis of the changes in detector signals in response to variations in analyte flow rate, to obtain useful information on the composition of analytes and analyte mixtures.

The dependence of the relative power spectral density on the volume of carbon black-polymer composite vapor detectors was of the form Sn?1/ V n, with n=1 for PEVA-carbon black detectors and n=0.6 for PCL-carbon black detectors in the frequency range of 1-800 Hz. Analytes with moderate polymer/gas partition coefficients produce the same DR/Rb response values on detectors of constant film thickness but of different area, so under these conditions the S/N is optimized for detectors of very large area. In contrast, for finite quantities of injected sample, analytes with high polymer/gas partition coefficients produce much larger DR/Rb values on detectors of small area that are positioned to best sample the injected analyte flow. For such detector/analyte combinations, detectors of small area will exhibit significantly better vapor detection sensitivity. Manipulation of the geometric form factor of carbon black-composite vapor detectors thus provides a facile method for optimizing the S/N performance for a particular detector/analyte combination of interest. An array of nominally identical polymer-carbon black detectors arranged linearly relative to the analyte flow path produces different spatiotemporal response patterns for analytes having different polymer/gas partition coefficients. Analytes with moderate polymer/gas partition coefficients produce the same signals on all detectors over a range of flow rates, whereas analytes with very large polymer/gas partition coefficients produce signals that are highly dependent on the analyte flow rate and the spatial position of the detector in the array. Such a configuration produces useful information on the composition of binary analyte mixtures and adds classification information to an array of compositionally different conducting polymer composite vapor detectors.

In addition, an array of 20 compositionally different carbon black-polymer composite chemiresistor vapor detectors was challenged under laboratory conditions to discriminate between a pair of extremely similar pure analytes (H2O and D2O), compositionally similar mixtures of pairs of compounds, and low concentrations of vapors of similar chemicals. Several discriminant algorithms were utilized, including k nearest neighbors (kNN, with k = 1), linear discriminant analysis (LDA, or Fisher's linear discriminant), quadratic discriminant analysis (QDA), regularized discriminant analysis (RDA, a hybrid of LDA and QDA), partial least squares (PLS), and soft independent modeling of class analogy (SIMCA). H2O and D2O were perfectly classified by most of the discriminants when a separate training and test set were used. As expected, discrimination performance decreased as the analyte concentration decreased, and performance decreased as the composition of the analyte mixtures became more similar. RDA was the overall best-performing discriminant, and LDA was the best-performing discriminant that did not require several cross-validations for optimization.